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Determination of 51 Priority Organic Compounds After Extraction from Standard Reference Materials

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16. ABSTRACT

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Determination of 51 Priority Organic Compounds after Extraction from Standard Reference Materials

Viorica Lopez-Avila,*[1] Raymond Northcutt, Jon Onstot, and Margie Wickham

Midwest Research Institute, 425 Volker Boulevard, Kansas City, Missouri 64110

Stephen Billets

U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Cincinnati, Ohio 45268

An extraction technique, involving homogenization of a sediment sample with dichloromethane at dual pH and phase separation by centrifugation, was used in the determination of 51 organic priority pollutants as identified in a standard reference sediment sample. These compounds were spiked into the sediment and equilibrated for a defined period of time. The extraction was performed first at pH >11 to isolate the base/neutral compounds; acidic compounds were extracted at pH <2. The extract containing the base/neutral compounds was fractionated by silica gel chromatography. The extract containing the acidic compounds was fractionated by gel permeation chromatography (GPC). Separation and identification of individual compounds in the silica gel fractions were accomplished by gas chromatography/mass spectrometry (GC/MS). Method precision and accuracy are discussed. Tentative identifications of other organic compounds found in the sediment are given.

Several extraction techniques including Soxhlet extraction (*1*), shaking (*2*), sonication (*3*), use of high-frequency mechanical dispersion (*4*), and steam distillation (*5*) have been used to isolate organic compounds from sediments. Mixtures of polar and nonpolar solvents are usually employed with the polar solvent added first to remove water from the sediment. Examples of such solvent pairs are acetone and dichloromethane (*6*), acetone and hexane (*7*), methanol and benzene (*8*), methanol and toluene (*9*), 2-propanol (*10*), etc. Soxhlet procedures were reported to give significantly greater recoveries than the sonication or steam distillation procedures (*11*); however, the evaluation was limited to PCB's and pesticides, and conclusions about the effectiveness of this technique when applied to a wider range of organic compounds could not be drawn.

While efficient extraction techniques are needed to isolate organic compounds from sediments, sample fractionation prior to gas chromatographic (GC) analysis and high-efficiency capillary columns are required to resolve the numerous components of a sediment extract. Common sample fractionation procedures prior to GC analysis involve: adsorption chromatography on silica gel (*12*), Florisil (*13*), cesium silicate (*14*), and/or gel permeation chromatography (*15*). Liquid–liquid partitioning procedures (*16*) have also been used.

With the recent development of the fused silica capillary columns that offer higher efficiency, improved peak shape, greater resolution, and inertness over the regular capillary columns, analysis of complex samples has been significantly improved. Furthermore, acidic and basic compounds can be analyzed on the same chromatographic column, either as separate fractions to avoid any possible chemical reactions or combined, in those cases when the combined extracts are shown to be chemically stable (*17*).

[1] Present address: Arthur Corp., 485 Clyde Av., Mountain View, CA 94042.

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Table I. Physicochemical Characterization of the NBS Sediment

Kjeldahl nitrogen	0.0797 ± 0.0048%
total phosphorus	0.051 ± 0.0014%
loss on ignition (800 °C)	10.72 ± 0.28%
oil and grease (Freon)	1.71 ± 0.26%
chemical oxygen demand (dichromate)	149400 ± 9000 mg/kg
mineralogical characterization	SiO_2, 51%; MgO, 4%; Al_2O_3, 4%; CaO, 4%
total organic carbon[a]	30000 mg/kg

[a] Measurement performed at Midwest Research Institute.

This paper repports on the application of an extraction procedure (*18*) for isolation of selected test compounds spiked into a sediment sample. The extraction procedure involved homogenization of a sediment/water slurry with dichloromethane at dual pH followed by centrifugation. A silica gel fractionation of the base/neutral extract and a gel permeation chromatography fractionation of the acidic extract were performed. The compounds selected for this study are 51 priority pollutants representative of nonpolar and polar compounds, basic and acidic compounds, and stable and reactive compounds. A standard reference sediment material available from the National Bureau of Standards was used as matrix.

EXPERIMENTAL SECTION

Sample Source. The standard reference sediment material was purchased from the National Bureau of Standards (NBS) and is identified as NBS Standard Reference Material No. 1645. According to NBS (*19*), the material was dredged from the bottom of the Indiana Harbor Canal near Gary, IN. The material was screened to remove foreign objects, freeze-dried, and sieved (particle size <180 μm). The material was sterilized by radiation to minimize biological activity. A gross characterization, done by NBS, is listed in Table I.

Reagents. The individual stock solutions for each of the 51 compounds (concentration approximately 4 mg/mL) were made in methanol, except for hexachlorobenzene, chrysene, and dibenz[*a*,*h*]anthracene stock solutions, which were made in tetrahydrofuran, and anthracene and benzo[*a*]pyrene, which were made in acetone. Internal standards naphthalene-d_8, anthracene-d_{10}, and chrysene-d_{12} were purchased from Merck, Sharp and Dohme, Stable Isotope Division (Quebec, Canada).

Sample Preparation. Figure 1 shows the sample preparation scheme. A 20-g aliquot of the NBS sediment was loaded into a 225-mL centrifuge bottle and diluted with 60 mL of purified water. The sample was homogenized with a Tekmar Tissumizer blending probe for 30 s to enhance the wetting of the sediment. The spike was added immediately following homogenization and allowed to equilibrate with the sediment for 24 h at 4 °C, using a mechanical device to tumble the sample continuously. Three sequential extractions with 80-mL aliquots of dichloromethane were performed first at pH >11 and then at pH <2. Following each addition of dichloromethane, the sample was homogenized for 30 s with a Tekmar Tissumizer blending probe, and centrifuged for 30 min at 2500 rpm to promote phase separation. Three distinct layers consisting of an aqueous layer on top, a dark solvent layer in the middle, and a firm solids layer on the bottom were observed. The base/neutral extracts were combined and dried by passage through a short column of anhydrous sodium sulfate prior to concentration to 5 mL in a Kuderna-Danish evaporator. Following extraction at pH >11, the sediment/water slurry was adjusted to pH <2 with 6 *N* hydrochloric acid, and the extraction, extract drying, and concentration steps were repeated to isolate the acidic compounds.

Cleanup of the base/neutral extracts was performed by silica gel chromatography, using 3% water deactivated silica (Silica Woelm, 70/150 mesh, ICN).

The elution patterns and the recoveries of the 42 base/neutral compounds from the silica gel column were determined in duplicate at two levels (8 μg, 80 μg per column), corresponding to the spiking levels in sediment samples. The compounds were loaded onto the silica gel column by mixing appropriate aliquots of the stock solution with 2.5 g of 3% water-deactivated silica gel in a 10-mL beaker. The solvent was removed under a gentle stream of dry nitrogen, and the adsorbent containing the spikes was transferred to the silica gel column. Four fractions were collected: fraction I eluted with 100 mL of hexane; fraction II eluted with 50 mL of 10% dichloromethane in hexane; fraction III eluted with 50 mL of 50% dichloromethane in hexane; fraction IV eluted with 150 mL of 5% acetone in dichloromethane. The sediment extracts were processed identically.

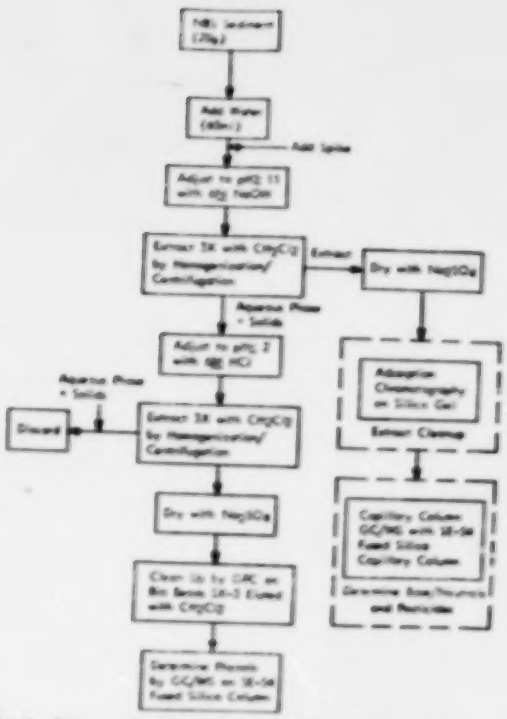

Figure 1. Scheme for the analysis of the NBS sediment.

Extracts containing the acidic compounds were fractionated by GPC with Biobeads SX-3 gels (BioRad, Inc.). The GPC column was calibrated with solutions of corn oil, *n*-butyl benzyl phthalate, and phenols (e.g., phenol, 2,4-dichlorophenol, and pentachlorophenol) following published procedures (*18*). The eluting solvent was dichloromethane. GPC recoveries of phenols were determined at 8 μg and 80 μg per column, corresponding to the spiking levels of the sediment samples.

Gas Chromatography and Gas Chromatography/Mass Spectrometry. A Varian 3700 gas chromatograph equipped with an effluent splitter and a fused silica capillary column (30 m × 0.25 mm i.d.) coated with SE-54 (film thickness 0.25 μm) was used for screening the various fractions prior to GC/MS analysis. The oven was held at 50 °C for 4 min during injection and then temperature programmed at 4 °C/min to 300 °C (10 min hold) for the base/neutral fractions. The oven was held at 60 °C for 5 min and temperature programmed at 8 °C/min to 325 °C for the acidic extracts. A flame ionization detector (FID) and an electron capture detector (ECD) were used simultaneously (effluent split ratio 1:1).

GC/MS analyses were performed on a Finnigan 4021 quadrupole mass spectrometer interfaced to a Finnigan 9600 gas chromatograph and operated under the control of an incos 2300 data system. All separations were performed by splitless injection using a SE-54 fused silica capillary column (30 m × 0.25 mm i.d.) connected directly to the ion source. The mass spectrometer was operated in the electron impact mode. Calibration of the mass spectrometer was checked daily, using decafluorotriphenylphosphine (DFTPP); resolution and focusing were adjusted to meet the DFTPP criteria (*20*). Emission current was in the 0.4–0.6 mA range, ionization energy was 70 eV, and the electron multiplier

Table II. Elution Patterns and Recoveries of Base/Neutral Compounds by Silica Gel Chromatography[a]

compound	fraction I hexane (100 mL)	fraction II 10% dichloromethane/ hexane (50 mL)	fraction III 50% dichloromethane/ hexane (50 mL)	fraction IV 5% acetone/ dichloromethane (150 mL)	total recovery, %
bis(2-chloroethyl) ether				+	95 ± 22
1,3-dichlorobenzene	+				64 ± 6
1,2-dichlorobenzene	+				67 ± 9
hexachloroethane	+				73 ± 14
N-nitrosodi-*n*-propylamine				+	94 ± 12
nitrobenzene			+	+	67 ± 3
bis(2-chloroethoxy)methane				+	66 ± 5
1,2,4-trichlorobenzene	+				70 ± 17
naphthalene	+	+	+		58 ± 7
hexachlorobutadiene	+				142 ± 51
hexachlorocyclopentadiene	+				300 ± 55
2-chloronaphthalene	+	+			94 ± 5
acenaphthylene		+	+		77 ± 21
2,6-dinitrotoluene				+	93 ± 19
acenaphthene		+	+		88 ± 12
2,4-dinitrotoluene				+	95 ± 14
fluorene				+	87 ± 22
4-chlorophenyl phenyl ether			+		109 ± 12
diethyl phthalate			+	+	90 ± 41
4-bromophenyl phenyl ether			+		116 ± 15
hexachlorobenzene	+				136 ± 23
phenanthrene			+		86 ± 30
anthracene			+		83 ± 23
di-*n*-butyl phthalate				+	80 ± 51
fluoranthene			+		51 ± 20
pyrene			+		63 ± 12
endosulfan sulfate				+	67 ± 17
n-butyl benzyl phthalate			+	+	87 ± 35
chrysene			+		72 ± 5
3,3′-dichlorobenzidine				+	40 ± 2
bis(2-ethylhexyl) phthalate				+	95 ± 61
benzo[*a*]pyrene			+		70 ± 34
dibenz[*a*,*h*]anthracene			+		84 ± 17
γ-BHC		+	+	+	66 ± 27
aldrin	+				67 ± 14
heptachlor epoxide			+	+	88 ± 3
p,*p*′-DDE	+	+	+		80 ± 6
endrin				+	77 ± 18
p,*p*′-DDD			+		78 ± 7
p,*p*′-DDT			+	+	91 ± 17
α-endosulfan			+	+	86 ± 17

[a] 3% deactivated silica gel. [b] Recoveries determined in duplicate at 5 μg and 80 μg levels for each compound; analyses done by fused silica capillary GC/MS.

was operated at 1.7 kV with the preamplifier set at 10^{-9} A/V.

Quality Assurance. Method blanks were performed for each step in the analysis. Except for bis(2-ethylhexyl) phthalate, none of the compounds reported in this paper have been detected in the method blanks. Levels reported for bis(2-ethylhexyl) phthalate have been corrected for the method blanks.

The fused silica capillary column was tested by using a standard test mixture containing 20 ng each of 2,6-dimethylphenol, 2,6-dimethylaniline, 1-octanol, 2-octanone, *n*-tridecane, *n*-tetradecane, and *n*-pentadecane; the number of effective plates (N_{eff}), peak asymmetry, column pH, separation number, and column adsorptivity were found to satisfy the acceptance criteria given elsewhere (*18*).

At the beginning of each day, a set of standards containing 42 base/neutral compounds and 9 acidic compounds at 5 ng/μL and 20 ng/μL was analyzed with each set of samples. The reproducibility of the relative retention time was ±0.1%. The percent relative deviation of the response factors was for most compounds less than 10%.

RESULTS AND DISCUSSION

Sample Preparation. The sample preparation technique described here was originally developed for publicly owned water treatment works (POTW) sludges (*18*). In order to be applied to the NBS sediment, an aliquot of the dry sediment is first slurried with water and then extracted with dichloromethane, using a high-speed homogenizer. Attention is called, however, to the fact that, if the sediment particles are not within a relatively narrow particle size range (e.g., 20–300 μm), then difficulties in isolating the organic layer from the aqueous and the solid layers will be experienced.

Although the evaluation experiments were conducted with a set of compounds representative of halogenated hydrocarbons, polycyclic aromatic hydrocarbons, phenols, etc. the results indicate that this extraction technique can be used to isolate other nonpolar and weakly polar compounds.

The cleanup of the base/neutral and the acidic fractions was performed by silica gel and gel permeation chromatography, respectively. Table II gives the elution patterns and the recoveries of base/neutral compounds. It can be noted that most of the halogenated hydrocarbons (e.g., dichlorobenzenes, trichlorobenzene, hexachlorobutadiene, hexachlorocyclopentadiene, hexachlorobenzene) elute in fraction I, whereas the polycyclic aromatic hydrocarbons (e.g., fluoranthene, pyrene, benzo[*a*]pyrene, dibenz[*a*,*h*]anthracene) elute in fraction III. The more polar compounds such as bis(2-chloroethyl) ether, *N*-nitrosodi-*n*-propylamine, bis(2-chloroethoxy)methane, dinitrotoluenes, and phthalates were identified in fraction IV. Several compounds (e.g., naphthalene, chloronaphthalene, γ-BHC, *p*,*p*′-DDE) were found

Table III. Recoveries of Phenols by Gel Permeation Chromatography

compound no.	compound	% recovery[a] 8 μg on column	% recovery[a] 80 μg on column
1	phenol	66	79
2	2-chlorophenol	67	82
3	2,4-dimethylphenol	59	69
4	2,4-dichlorophenol	56	79
5	2,4,6-trichlorophenol	72	86
6	2,4-dinitrophenol	0	112
7	4-nitrophenol	45	91
8	4,6-dinitro-o-cresol	0	126
9	pentachlorophenol	42	86

[a] % recovery determined from single measurement.

to spread over two or three silica gel fractions; however, only one of the fractions contained at least 75% of the amount spiked. Data in Table II also indicate that with a few exceptions the recoveries of the base/neutral compounds are quantitative and reproducible. The poor chromatographic behavior of hexachlorobutadiene and hexachlorocyclopentadiene resulted in excessively high recovery values. It is not known whether benzidine was present in any of the silica gel fractions since it could not be detected by GC/MS at levels ≤20 ng per injection.

Table III gives the recovery data for phenols. All phenols were recovered from spiked blanks at both spike levels. The chromatographic behavior of dinitrophenols may have precluded their identification at levels below 8 ng/μL in the GPC fractions. Due to these problems, these compounds were not reported for the spiked sediment (Table V).

Method Precision and Accuracy. The results of the precision and accuracy determinations for the base/neutral compounds are given in Table IV. Of all recovery determinations in Table IV, 51% fell within the range 60–120%. An additional 16% were below 60% recovery, and 8% were above the 120% recovery. Due to the high concentrations of several compounds in the unspiked sediment, their recoveries could not be determined at the lower spike level. For example, fluoroanthene, pyrene, chrysene, and benzo[a]pyrene had levels above 10 000 ng/g of dry sediment. Furthermore, because of the complexity of the sediment sample, coeluting compounds may have also contributed to the high standard deviations of the recoveries of many of the spikes and the very poor recoveries of several compounds in Table IV. Polar and reactive compounds such as hexachlorocyclopentadiene, benzidine, 3,3'-dichlorobenzidine, heptachlor epoxide (only at 400 ng/g of dry sediment), endrin, and α-endosulfan were not recovered.

The results of the precision and accuracy determinations for the acidic compounds are given in Table V. Of all recovery determinations, 64% were greater than 70%, 29% were between 40% and 70%, and 7% were zero. Quantitative recoveries (>70%) were found at both spike levels for phenol, 2-chlorophenol, 2,4-dichlorophenol, 2,4-dimethylphenol, and pentachlorophenol. 4-Nitrophenol was not detected at 400 ng/g; however its recovery was satisfactory at the higher spike level. The chromatographic behavior of this compound may have precluded its identification at low spike levels.

Identification of Compounds in the NBS Sediment Extract. The GC/MS analyses of the silica gel fractions and the GPC fraction generated from the NBS sediment extract resulted in the identification of over 100 base/neutral compounds and 11 acidic compounds, without considering the various isomers of many of these compounds. Table VI gives these identifications, grouped by chemical class. Figures 2–5 give the GC/MS chromatograms of the various fractions.

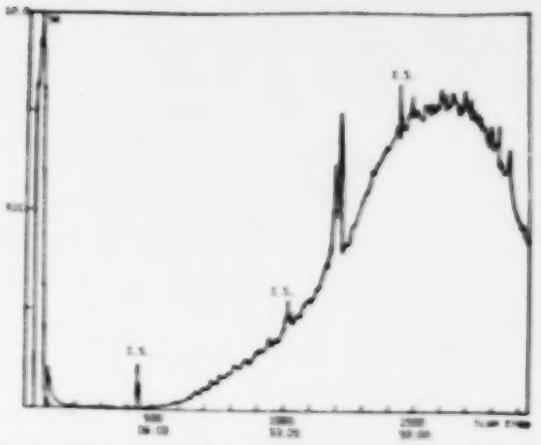

Figure 2. Reconstructed ion chromatogram of fraction I of base/neutral extract (silica gel chromatography; eluting solvent, hexane). Temperature was programmed from 50 °C (held 4 min) to 300 °C at 4 °C/min. I.S. is the internal standard.

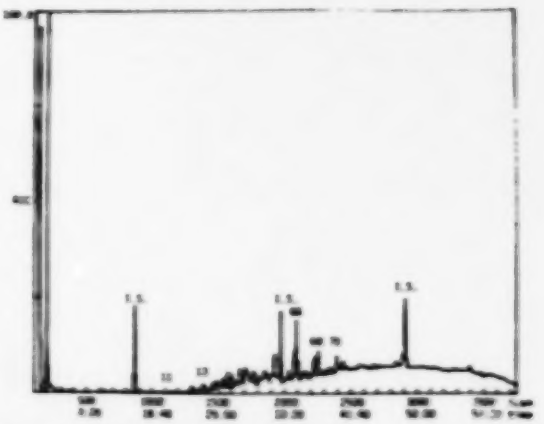

Figure 3. Reconstructed ion chromatogram of fraction II of base/neutral extract (silica gel chromatography; eluting solvent, 10% dichloromethane in hexane). Temperature was programmed from 50 °C (held 4 min) to 300 °C at 4 °C/min. Peak assignments are given in Table VI.

Because authentic reference standards were not analyzed for each compound, the identifications are tentative except for some compounds given in Table VI that were confirmed with standards. Most of the compounds listed in Table VI give mass spectra that matched the mass spectra in the NBS library (*21*). Identification of specific positional isomers (e.g., dimethylnaphthalenes, trimethylnaphthalenes, etc.) could not be obtained from the mass spectrometric information.

The procedures used to identify each GC peak involved selection of a background substracted mass spectrum and the comparison of this mass spectrum against that contained in the NBS library. The computer search provided the match indexes (e.g., for Incos software FIT, PURITY, and RFIT indexes) that were used in identifying the compounds. Many of the mass spectra were also manually interpreted, especially when a match via library search was unsuccessful.

A limiting factor in the mass spectra identifications was the purity of a compound (coeluting peaks would give mass spectra with large FIT indexes but low PURITY indexes) and the availability of the compound mass spectrum in the data base. Whenever an identification was made, either by library search routines or by manual interpretation, mass chromatograms for the most intense ions in the mass spectrum were obtained. This allowed in many instances identification of other isomers and assignment of coeluting peaks. Although the library

Table IV. Results of the Precision and Accuracy Evaluations for the Analysis of Base/Neutral Compounds in the Spiked NBS Sediment

compound no.	compound	unspiked sediment[a] concn (ng/g of dry sediment)	% recovery[a] spike level 400 ng/g of dry sediment	% recovery[a] spike level 4000 ng/g of dry sediment
1	bis(2-chloroethyl) ether	ND[e]	96 ± 23	112 ± 19
2	1,3-dichlorobenzene	ND	63 ± 9	68 ± 16
3	1,2-dichlorobenzene	ND	66 ± 14	75 ± 22
4	hexachloroethane	ND	41 ± 15	62 ± 5
5	*N*-nitrosodi-*n*-propylamine	ND	95 ± 38	89 ± 11
6	nitrobenzene	ND	43 ± 3	102 ± 26
7	bis(2-chloroethoxy)methane	ND	94 ± 39	81 ± 11
8	1,2,4-trichlorobenzene	ND	67 ± 4	58 ± 13
9	naphthalene	880 ± 350	64[c]	70 ± 35
10	hexachlorobutadiene	ND	63 ± 2	71 ± 17
11	hexachlorocyclopentadiene	ND	0	0
12	2-chloronaphthalene	ND	72 ± 10	94 ± 20
13	acenaphthylene	1820 ± 350	[d]	86 ± 24
14	2,6-dinitrotoluene	ND	110 ± 51	102 ± 36
15	acenaphthene	850 ± 120	[d]	104 ± 24
16	2,4-dinitrotoluene	ND	49[c]	64 ± 50
17	fluorene	1580 ± 120	[d]	82 ± 7
18	4-chlorophenyl phenyl ether	ND	86 ± 42	74 ± 7
19	diethyl phthalate	ND	33 ± 14	109 ± 13
20	4-bromophenyl phenyl ether	ND	91 ± 50	89 ± 2
21	hexachlorobenzene	ND	46 ± 10	53 ± 4
22	phenanthrene	3770 ± 300	[d]	83 ± 26
23	anthracene	2090 ± 72	[d]	25 ± 11
24	di-*n*-butyl phthalate	580 ± 65	156[c]	100, 137
25	fluoranthene	14760 ± 2810	[d]	174 ± 76
26	pyrene	20020 ± 4630	[d]	140, 252
27	benzidine[b]	ND	0	0
28	endosulfan sulfate	1160, 455	97, 137	0
29	*n*-butyl benzyl phthalate	920	[d]	103[c]
30	chrysene	27000 ± 6500	[d]	[d]
31	3,3′-dichlorobenzidine	ND	0	0
32	bis(2-ethylhexyl) phthalate	7560, 10790	[d]	[d]
33	benzo[*a*]pyrene	22850 ± 6200	[d]	128 ± 23
34	dibenz[*a*,*h*]anthracene	5960 ± 420	[d]	113 ± 42
35	γ-BHC	2050 ± 1270	[d]	60 ± 19
36	aldrin	ND	44[c]	22 ± 13
37	heptachlor epoxide	ND	0	54 ± 9
38	*p,p*′-DDE	340 ± 100	41[c]	76 ± 32
39	endrin	ND	0	0
40	*p,p*′-DDD	120	121, 186	104 ± 18
41	*p,p*′-DDT	840 ± 20	[d]	155 ± 43
42	α-endosulfan	ND	0	0

[a] Mean ± standard deviation for three determinations; % recovery = (spiked sed. concn − unspiked sed. concn)/spike level. [b] Benzidine not detected by GC/MS in any of the standards at concentrations < 20 ng per injection. [c] Single determination reported; levels in the other replicates were below the unspiked sediment level. [d] Concentrations determined in the spiked sediment were below the unspiked sediment level. [e] Not detected.

Table V. Results of the Precision and Accuracy Evaluations for the Analysis of Acidic Compounds in the Spiked NBS Sediment

compound no.	compound	unspiked sediment concn (ng/g of dry sediment)	% recovery[a] spike level 400 ng/g of dry sediment	% recovery[a] spike level 4000 ng/g of dry sediment
1	phenol	1810, 2005	112, 128	78 ± 21
2	2-chlorophenol	ND[b]	106 ± 11	78 ± 18
3	2,4-dimethylphenol	ND	99 ± 12	55 ± 3
4	2,4-dichlorophenol	ND	99 ± 16	76 ± 5
5	2,4,6-trichlorophenol	ND	67 ± 8	63 ± 10
6	4-nitrophenol	ND	0	46 ± 11
7	pentachlorophenol	ND	95 ± 2	71 ± 3

[a] % recovery determined from triplicate measurements; recovery = spiked sed. concn − unspiked sed. concn/ spike added. [b] Not detected.

search did indicate in many cases the positional isomers that best match a particular unknown mass spectrum, this was not sufficient for confirming the compound identity. Consequently, no indication about the position of the substituent or the particular alkyl radical has been made.

Fractionation of the base/neutral extract by silica gel chromatography reduced sample complexity and, consequently, made possible identification of minor components

Table VI. Organic Compounds Identified in the NBS Sediment

compound no.	compound	silica gel fractions[b]			
		I	II	III	IV
	Aliphatic Hydrocarbons				
1	heptane				
2	$C_{12}H_{26}$ (isomers)		X		
3	$C_{13}H_{28}$ (isomers)		X		
			X		
	Aromatic Hydrocarbons				
4	benzene				
5	toluene		X		
6	xylene (isomers)		X		
7	C_3-alkylbenzene		X		
8	styrene		X		
					X
	Polycyclic Aromatic Hydrocarbons				
9	naphthalene[a]				
10	1-methylnaphthalene		X	X	
11	2-methylnaphthalene		X	X	
12	ethylnaphthalene		X	X	
13	dimethylnaphthalene (isomers)		X	X	
14	C_3-alkylnaphthalene (isomers)		X	X	
15	C_4-alkylnaphthalene (isomers)		X	X	
16	C_5-alkylnaphthalene (isomers)		X		
17	1-phenylnaphthalene		X		
18	2-phenylnaphthalene			X	
19	phenylmethylnaphthalene (isomers)			X	
20	acenaphthylene[a]			X	
21	biphenyl	X	X	X	X
22	terphenyl			X	
23	acenaphthene[a]			X	
24	diphenyl ether		X	X	X
25	fluorene[a]		X		
26	methylfluorene (isomers)			X	X
27	dimethylfluorene (isomers)			X	
28	C_3-alkylbiphenyl			X	
29	phenanthrene[a]			X	
30	anthracene[a]		X	X	X
31	methylphenanthrene (isomers)		X	X	X
32	methylanthracene (isomers)			X	
33	ethylphenanthrene or ethylanthracene			X	
34	dimethylphenanthrene (isomers)			X	
35	dimethylanthracene (isomers)			X	
36	C_3-alkylphenanthrene (isomers)			X	
37	C_3-alkylanthracene (isomers)			X	
38	4*H*-cyclopenta[*def*]phenanthrene			X	
39	fluoranthene[a]			X	
40	pyrene[a]			X	X
41	methylfluoranthene (isomers)		X	X	X
42	methylpyrene (isomers)			X	
43	benzphenanthrene (isomers)			X	
44	benzanthracene (isomers)			X	
45	chrysene[a]			X	
46	methylbenzanthracene (isomers)			X	X
47	methylchrysene (isomers)			X	
48	dimethylbenzanthracene (isomers)			X	
49	dimethylchrysene (isomers)			X	
50	dimethyltriphenylene (isomers)			X	
51	1,1′-binaphthyl			X	
52	1,2′-binaphthyl			X	
53	2,2′-binaphthyl			X	
54	benzofluoranthene (isomers)			X	
55	benzo[*a*]pyrene[a]			X	
56	perylene			X	X
57	methylbenzofluoranthene (isomers)			X	
58	methylbenzopyrene (isomers)			X	
59	dibenzoanthracene (isomers)			X	
60	benzochrysene (isomers)			X	
61	dibenz[*a,h*]anthracene[a]			X	
62	benzo[*ghi*]perylene			X	X
63	indeno[1,2,3-*cd*]pyrene			X	
				X	
	Sulfur-Containing Heterocyclics				
64	di-*n*-propylthiophene (isomers)				
65	dibenzothiophene			X	
66	methyldibenzothiophene (isomers)		X	X	
67	dimethyldibenzothiophene (isomers)		X	X	X
68	dimethylnaphthothiophene (isomers)		X	X	
69	ethylnaphthothiophene		X	X	
			X		

Table VI (*Continued*)

compound no.	compound	silica gel fractions[b] I	II	III	IV
70	C_1-alkyldibenzothiophene		X		
71	C_2-alkyldibenzothiophene		X		
72	benzonaphthothiophene (isomers)			X	
73	methylbenzonaphthothiophene (isomers)			X	
74	benzophenanthrenothiophene			X	
75	anthrabenzothiophene			X	
76	$C_{17}H_{10}S$ (isomers)			X	
77	dinaphthothiophene (isomers)			X	
78	thioxanthene			X	
	Oxygen-Containing Heterocyclics				
79	methyldibenzofuran (isomers)			X	
	Aldehydes and Ketones				
80	benzaldehyde				X
81	1-phenylethanone				X
82	fluorenone				X
83	methylfluorenone (isomers)				X
84	methylanthrone (isomers)				X
85	cyclopenta[*def*]phenanthrenone				X
86	benzofluorenone (isomers)				X
87	methylbenzofluorenone (isomers)				X
88	benzanthracenequinone (isomers)				X
89	indenoanthracenone (isomers)				X
90	$C_{19}H_{12}O$ (isomers)				X
	Pesticides				
91	*p,p'*-DDE[a]			X	
92	*p,p'*-DDD[a]				X
93	*p,p'*-DDT[a]		X	X	
94	γ-BHC[a]		X		
	Phenols				
95	phenol[a]				
	Miscellaneous Compounds				
96	benzoic acid				
97	ethylhexanol				X
98	1-(2-propenyloxy)heptane				X
99	acetic acid phenylethyl ester				X
100	1-*H*-indene				X
101	di-*n*-butyl phthalate[a]	X		X	X
102	*n*-butyl benzyl phthalate[a]				X
103	bis(2-ethylhexyl) phthalate[a]			X	X
104	endosulfan sulfate[a]				X
105	methylcholestane				X
106	$C_{28}H_{46}O$ (possible ergosta-5,8-diene-3-ol)		X		
107	sulfur	X			
108	fatty acids				

[a] Confirmed with authentic compounds. [b] Silica gel fractions: I, hexane; II, 10% dichloromethane/hexane; III, 50% dichloromethane/hexane; IV, 5% acetone/dichloromethane.

in the sample. Furthermore, the chromatographic behavior on silica gel of several classes of compounds (e.g., sulfur containing heterocyclics, aldehydes, ketones) helped in the assignment of the identifications.

For example, polar compounds such as benzofluorenone and methylbenzofluorenone were expected to elute in fraction IV. Indeed, benzofluorenone (m/z 230) was identified by reverse library search in fraction IV; however, no mass spectral match was found for the mass spectrum with a parent ion at m/z 244. The assignment as methylbenzofluorenone for mass spectrum with a parent at m/z 244 was based on two considerations: similar mass spectral fragmentation pattern with benzofluorenone and similar chromatographic behavior on silica gel of benzofluorenone and methylbenzofluorenone.

The GC/MS chromatograms given in Figures 2–5 also show that most of the compounds of environmental significance elute in fractions II and III (the compound numbers in Table VI correspond to the labeled peaks in Figures 2–5). Fraction I contains mostly saturated hydrocarbons (alkanes) that were not resolved under the conditions used. Similarly, fraction IV contains polar compounds (naturally occurring materials) that would interfere in the analysis, had the sample fractionation not been performed.

CONCLUSIONS

The method described offers a rapid means of analyzing for organic compounds in a sediment matrix. Given the complexity of this matrix, the precision and accuracy results presented here demonstrate that the extraction procedure developed originally for sludge matrices can be applied with minor modifications to sediments. Fractionation of the base/neutral extract by silica gel chromatography and fractionation of the acidic extract by GPC are required to reduce sample complexity and have been evaluated at two concentration levels for 51 priority organic compounds. Quantitative and reproducible recoveries were demonstrated for stable compounds such as chlorinated benzenes, polynuclear aromatic hydrocarbons, bis(2-chloroethyl) ether, *p,p'*-DDD, and *p,p'*-DDT at both spike levels while polar and reactive compounds were not recovered.

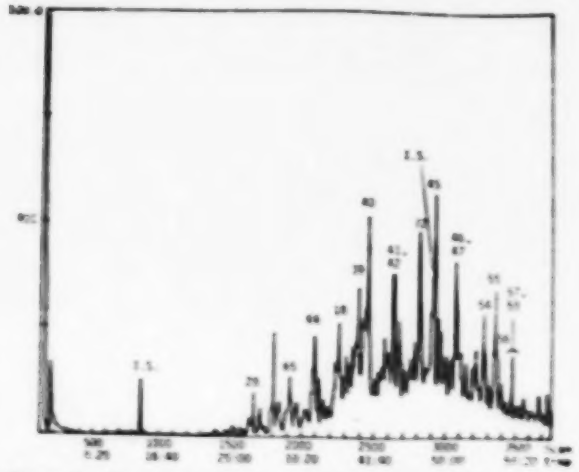

Figure 4. Reconstructed ion chromatogram of fraction III of base/neutral extract (silica gel chromatography; eluting solvent, 50% dichloromethane in hexane). Temperature was programmed from 50 °C (held 4 min) to 300 °C at 4 °C/min. Peak assignments are given in Table VI.

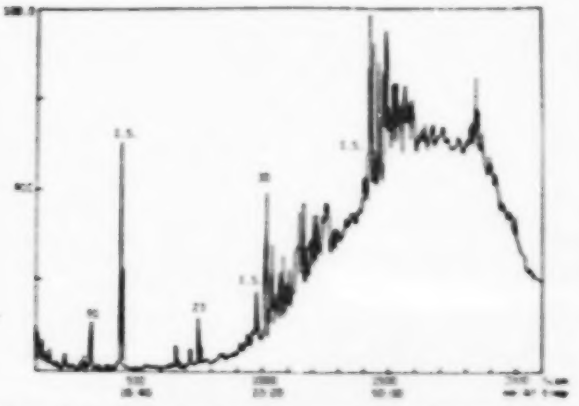

Figure 5. Reconstructed ion chromatogram of fraction IV of base/neutral extract (silica gel chromatography; eluting solvent, 5% acetone in dichloromethane). Temperature was programmed from 50 °C (held 4 min) to 300 °C at 4 °C/min. Peak assignments are given in Table VI.

The inertness and excellent resolution of the capillary column allowed the detection of nanogram levels of phenols in the presence of high levels of interfering coextractants. Furthermore, tentative identifications were provided for the organic compounds extracted from sediment by the extraction and analysis procedures described in this paper. Most of the compounds identified in the silica gel and GPC fractions were polycyclic aromatic hydrocarbons, alkyl-substituted polyaromatics, sulfur-containing heterocyclics, alkyl-substituted sulfur-containing heterocyclics, and several polycyclic ketones.

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Registry No. Bis(2-chloroethyl) ether, 111-44-4; 1,3-dichlorobenzene, 541-73-1; 1,2-dichlorobenzene, 95-50-1; hexachloroethane, 67-72-1; *N*-nitrosodi-*n*-propylamine, 621-64-7; nitrobenzene, 98-95-3; bis(2-chloroethoxy)methane, 111-91-1; 1,2,4-trichlorobenzene, 120-82-1; naphthalene, 91-20-3; hexachlorobutadiene, 87-68-3; hexachlorocyclopentadiene, 77-47-4; 2-chloronaphthalene, 91-58-7; acenaphthylene, 208-96-8; 2,6-dinitrotoluene, 606-20-2; acenaphthene, 83-32-9; 2,4-dinitrotoluene, 121-14-2; fluorene, 86-73-7; 4-chlorophenyl phenyl ether, 7005-72-3; diethyl phthalate, 84-66-2; 4-bromophenyl phenyl ether, 101-55-3; hexachlorobenzene, 118-74-1; phenanthrene, 85-01-8; anthracene, 120-12-7; di-*n*-butyl phthalate, 84-74-2; fluoranthene, 206-44-0; pyrene, 129-00-0; benzidene, 92-87-5; endosulfan sulfate, 1031-07-8; *n*-butylbenzyl phthalate, 85-68-7; chrysene, 218-01-9; 3,3'-dichlorobenzidine, 91-94-1; bis(2-ethylhexyl) phthalate, 117-81-7; benzo[*a*]pyrene, 50-32-8; dibenz[*a,h*]anthracene, 53-70-3; γ-BHC, 58-89-9; aldrin, 309-00-2; heptachlor epoxide, 1024-57-3; *p,p'*-DDE, 72-55-9; endrin, 72-20-8; *p,p'*-DDD, 72-54-8; *p,p'*-DDT, 50-29-3; α-endosulfan, 959-98-8; phenol, 108-95-2; 2-chlorophenol, 95-57-8; 2,4-dimethylphenol, 105-67-9; 2,4-dichlorophenol, 120-83-2; 2,4,6-trichlorophenol, 88-06-2; 2,4-dinitrophenol, 51-28-5; 4-nitrophenol, 100-02-7; 4,6-dinitro-o-cresol, 534-52-1; pentachlorophenol, 87-86-5; heptane, 142-82-5; benzene, 71-43-2; toluene, 108-88-3; xylene, 1330-20-7; styrene, 100-42-5; 1-methylnaphthalene, 90-12-0; 2-methylnaphthalene, 91-57-6; ethylnaphthalene, 27138-19-8; dimethylnaphthalene, 28804-88-8; 1-phenylnaphthalene, 605-02-7; 2-phenylnaphthalene, 612-94-2; phenylmethylnaphthalene, 71697-04-6; biphenyl, 92-52-4; terphenyl, 26140-60-3; diphenyl ether, 101-84-8; methylfluorene, 26914-17-0; dimethylfluorene, 30582-01-5; methylphenanthrene, 31711-53-2; methylanthracene, 613-12-7; dimethylphenanthrene, 29062-98-4; dimethylanthracene, 29063-60-1; 4*H*-cyclopenta[*def*]phenanthrene, 203-64-5; methylfluoranthene, 30997-39-8; methylpyrene, 27577-90-8; benzphenanthrene, 65777-08-4; benzanthracene, 56-55-3; methylbenzanthracene, 43178-22-9; methylchrysene, 41637-90-5; dimethylbenzanthracene, 57-97-6; dimethylchrysene, 41637-92-7; dimethyltriphenylene, 60826-76-8; 1,1'-binaphthyl, 604-53-5; 1,2'-binaphthyl, 4325-74-0; 2,2'-binaphthyl, 612-78-2; benzofluoranthene, 56832-73-6; perylene, 198-55-0; methylbenzofluoranthene, 73020-30-1; methylbenzopyrene, 65357-69-9; dibenzoanthracene, 67775-07-9; benzochrysene, 57827-84-6; benzo[*ghi*]perylene, 191-24-2; indeno[1,2,3-*cd*]pyrene, 193-39-5; di-*n*-propylthiophene, 84987-78-0; dibenzothiophene, 132-65-0; methyldibenzothiophene, 30995-64-3; dimethyldibenzothiophene, 70021-47-5; benzonaphthothiophene, 61523-34-0; dinaphthothiophene, 71012-24-3; thioxanthene, 261-31-4; methyldibenzofuran, 60826-62-2; benzaldehyde, 100-52-7; 1-phenylethanone, 98-86-2; fluorenone, 84987-80-4; methylfluorenone, 79147-47-0; methylanthrone, 79073-29-9; cyclopenta[*def*]phenanthrenone, 5737-13-3; benzofluorenone, 76723-60-9; benzoic acid, 65-85-0; ethylhexanol, 75737-89-2; 1-(2-propenyloxy)heptane, 16519-24-7; acetic acid phenylethyl ester, 103-45-7; 1-*H*-indene, 95-13-6.

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